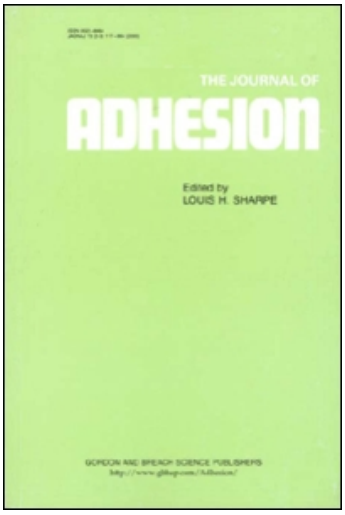

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Optimization of Surface Treatment and Adhesive Selection for Bond Durability in Ti-15-3 Laminates

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The promising mechanical performance of a baseline Hybrid Titanium Composite Laminate (HTCL) inspired an investigation into maximizing the strength and environmental performance of this new aerospace material. This research focused upon finding the strongest and most durably combination of three commercially-available titanium surface treatments (*i.e.*, Pasa-Jell 107™, Boeing's Sol-Gel, and Turco 5578®) and two polyimide adhesives (*i.e.*, LaRC™-IAX and FM5®) for use in HTCL. The tests employed the cracked-lap shear (CLS) specimen geometry for fatigue crack growth measurements and also for fracture toughness analyses of the bonded specimens. The CLS geometry models several bonded applications found in the aerospace industry, and it also represents the debonding characteristics of a cracked titanium foil in HTCL.

The environmental performance of these six material combinations has been evaluated after 5,000 hours of continuous exposure to either a Hot/Wet environment that subjected the bonded specimens to 160°F (71°C) with relative humidity in excess of 95%, or to a Hot/Dry environment of 350°F (177°C) with a relative humidity of less than 5%. These two exposure environments utilized in this study are the most aggressive long-term environments that the HTCL is projected to experience while in service.

Test results showed that the best combination of the titanium surface treatments and the polyimide adhesives in the FM5® adhesive used in conjunction with Boeing's Sol-Gel titanium surface treatment. Though the FM5®/Sol-Gel system was the strongest of all combinations, its performance dropped to less than 50% of its original strength after exposure to the Hot/Dry environment. An important finding is that this bonded system did not significantly degrade after exposure to the Hot/Wet environment. The only other material combination that showed substantial bond strength was the FM5®/Pasa-Jell 107 system, though its strength also dropped to less than 50% of its original strength after exposure to the Hot/Dry environment.

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Keywords: Titanium bonding; polyimide adhesive; titanium surface treatment; high temperature bonding; titanium composite; hybrid titanium composite laminate; titanium graphite reinforced laminate; adhesive durability; aerospace bonding

INTRODUCTION

In the realm of aerospace design and performance, there are few boundaries in the never-ending drive for increased performance. This thirst for ever-increased performance of aerospace equipment has driven the aerospace and defense industries into developing exotic, extremely high-performance composites that are pushing the envelope in terms of strength-to-weight ratios, durability, and several other key properties.

To meet this challenge of ever-increasing improvement, engineers and scientists at NASA-Langley Research Center (NASA-LaRC™) have developed a high-temperature metal laminate based upon titanium, carbon fibers, and a thermoplastic resin [1]. A schematic of this laminate is shown in Figure 1. This composite, known as the Hybrid Titanium Composite Laminate, or HTCL, is the latest chapter in a significant, but relatively short, history of metal laminates. During the mid-1960s, Kaufman [2] showed that it was possible to improve the fracture toughness of aluminum by laminating thin plies of aluminum

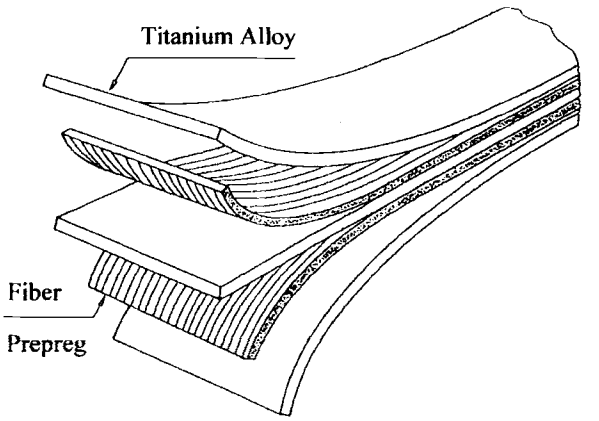

FIGURE 1 Schematic of a typical HTCL construction.

together. During the latter half of the 1970s, Johnson and colleagues [3, 4] demonstrated that adhesively laminating thin aluminum plies together would dramatically improve the fatigue resistance along with improving the crack growth resistance. In the early 1980s, Johnson followed upon his earlier findings to show that adhesively-laminated titanium plies improved fracture toughness by almost 40%, increased fatigue life by an order or magnitude, and reduced through-the-thickness crack growth rates by 20% over an equivalent monolithic titanium plate [5].

The next advancement in the history of metal laminates was made at Delft University, in the Netherlands, in conjunction with Alcoa. In the mid-1980s researchers at Delft University investigated the performance improvements offered by the ARALL family of fiber-reinforced metal laminates. The ARALL laminates included aramid fibers in the adhesive bondline between the aluminum plies, further improving the mechanical properties of the laminate [6, 7].

The HTCL family of metal laminates took the concept of adding fibers to the adhesive bondline and applied it to materials in the high-temperature regime of supersonic flight. The high temperatures found in supersonic flight necessitate the use of titanium rather than aluminum, and the substitution of the adhesive with an adhesive that could withstand the higher operating temperature for extended periods of time.

Traditional polymeric matrix composites (PMCs) have demonstrated very good stiffness-to-weight performance as well as superior fatigue resistance when compared with traditional metal alloys. But, due to the nature of the polymer matrix, some properties such as bolt-bearing capacity and lightning-strike protection are reduced in comparison with traditional metal alloys. In addition, current PMCs are not useful in the temperature ranges required for supersonic aircraft. To overcome these issues, the HTCL family of laminates was developed, and they have shown great potential in initial studies.

EARLY FINDINGS

In preliminary research performed by Miller *et al.* [1] at NASA-LaRC™, the first topic that was examined was the mechanical

properties of HTCL. Using Ti-6Al-4V (Ti-6-4) titanium alloy, IM7 carbon fibers (Hexcel Corp., Pleasanton, CA), and LaRC^{TM}-IA polyimide as the constituent materials in the HTCL, the monotonic and fatigue properties of this laminate were determined. The polyimide adhesive and the IM7 carbon fibers were essentially a polymer matrix composite (PMC) layer that also served as an adhesive for the titanium foils. The Ti-6-4 foils were treated with Pasa-Jell 107^{TM} (SEMCO, Glendale, CA), which produces a micro-rough surface on the titanium foil. This micro-rough surface improves the durability and strength of the adhesive bond. The initial stress-strain response of the HTCL laminate was determined at room temperature and compared with the response of monolithic titanium. Miller *et al.*, found that the performance of the HTCL was dependent upon processing methods and procedures used.

To develop some predictive techniques for HTCLs, the AGLPLY laminate code was employed. The AGLPLY code, written by Bahei-El-Din, was originally developed to analyze metal matrix composites, based upon constituent properties. It had demonstrated good predictive ability for metal matrix composites, so its predictive ability was evaluated for this laminate. The AGLPLY code performs an elastic-plastic analysis of symmetric laminated plates under in-plane mechanical loads (non-bending). The lamina properties are calculated *via* the vanishing fiber diameter (VFD) model; this model assumes a rule of mixtures contribution of the fiber modulus to the composite modulus in the longitudinal direction, but it does not allow for any transverse constraint by the fiber. AGLPLY calculates the overall laminate elastic moduli and the local fiber and matrix stresses and strains in each ply, as well as the overall laminate strains for the entire elastic-plastic loading regime.

After the static stress-strain performance was evaluated, specimens of HTCL and of Ti-6-4 were fatigued at a constant amplitude with an R-ratio of $R = 0.1$ and at a frequency of 10 Hz. These fatigue specimens were straight-sided, containing a center hole. The applied fatigue loads were calculated by using an equivalent load-to-weight ratio for the HTCL and the Ti-6-4 specimens. The tests revealed that the HTCL displayed a dramatic increase in fatigue life of almost two orders of magnitude, when compared with monolithic titanium. This

trend occurred both at room temperature and at elevated temperature fatigue tests.

PRIOR WORK: HTCL MECHANICAL CHARACTERIZATION

Parametric Study

From these promising data, Li *et al.* [8] began a systematic study of HTCL to determine the optimal combination of constituent materials, material volume fractions, and processing techniques. Li *et al.*, first performed a parametric analysis of HTCL with the AGLPLY laminate code. They investigated the effect of various fibers, fiber orientation, and the effect of different metastable titanium β-alloys on the mechanical per- formance of the laminate. In addition, Li *et al.*, varied the volume fraction of each constituent in the laminate. This parametric study focused on predicting the laminate stress-strain curve up to the failure point for each combination of constituent materials and volume fractions.

The AGLPLY laminate code output closely correlated the stress-strain response of the HTCL laminate investigated by Miller *et al.* [1]. This good correlation helped validate the subsequent use of the AGLPLY laminate code in other analyses of HTCL. Using the stress-strain performance of each constituent material, the output from the AGLPLY laminate code provided insight into the performance of various HTCL lay-ups. As expected, the fiber properties had a pronounced influence upon the stress-strain response of HTCL.

The comparison made between various fiber orientations in HTCL found that the titanium foils made the HTCL much more isotropic without reducing the potential for high stiffness. In fact, the HTCL is nearly as stiff as the PMC in the fiber direction, but the HTCL modulus is more than ten times as great as the PMC modulus in the transverse direction.

Fatigue Properties and Damage Mechanisms

After completing the parametric study, Li and Johnson [9] examined the fatigue properties of HTCL and of the titanium foils used in HTCL.

The HTCL that was used in these fatigue tests was a "baseline" laminate that consisted of thin titanium foils with LaRC^{TM}-IAX polymide adhesive and IM7 carbon fibers forming a PMC layer between the titanium foils. To improve the bond strength of the titanium to the LaRC^{TM}-IAX adhesive, the Pasa-Jell 107^{TM} surface treatment was applied to the titanium foils.

The fatigue tests in Li and Johnson's study used straight-sided specimens for tests at room temperature, and also at 350°F (177°C). The HTCL specimens were cycled at an R-ratio of 0.1, and various load levels, to produce the fatigue profiles. From these tests, the endurance limit, or maximum stress at 1×10^6 cycles, was greater than 100 ksi. This is approximately a 10% increase above the fatigue strength of the monolithic titanium alloy.

An important discovery made during fatigue testing was that the endurance limit actually *increased* slightly at an elevated temperature of 350°F (177°C). This endurance limit increase is primarily due to two factors: 1) the laminate realized a reduction in residual stress between the titanium foils and the PMC layers at higher operating temperatures, and 2) the titanium alloy showed an improvement in toughness at elevated temperatures.

During fatigue, the progression of damage in the laminate occurs with the development of cracks in the outer titanium foils, and subsequent failure of the PMC layers through the thickness of the specimen. The PMC layers provide a damage-tolerant mechanism by shielding adjacent titanium plies from the cracked ply. The ply-by-ply failure of the titanium foils requires a re-initiation of the crack at each titanium-polymer interface, thereby providing a fatigue-resistant mechanism for the HTCL. Once the titanium ply is cracked, the applied stress that it was supporting is then transferred to the PMC layers, increasing the stress on the PMC. The failure of the entire HTCL is predicated by the failure of a sufficient number of the PMC layers, which occurs if the applied stress is large enough.

The absence of polymer on the titanium foils indicated that the interfacial strength was lower than the cohesive strength of the polymer, so the failure was between the PMC and the titanium foil instead of within the PMC. It is important to note that the HTCL can still carry a substantial fatigue load if that load is below the ultimate strength of the PMC layers, even when all of the titanium plies are cracked and carrying no load.

PRESENT WORK: DURABILITY OF HTCL

In Li and Johnson's work, some important issues surfaced during fatigue testing regarding the failure modes and damage mechanisms of HTCL. The extensive delamination observed during fatigue failure indicated that the bond strength between the titanium and the polyimide should be optimized to provide the desired amount of delamination. Also, durability issues regarding the titanium-polyimide bond needed to be examined after long-term exposure in elevated temperatures and also in hot, humid environments.

The primary method to improve bond strength and durability is to prepare the surface of the titanium. The surface treatment produces a relatively continuous micro-rough surface on the titanium foil, which improves the mechanical interlocking between the titanium and the polyimide. The improved mechanical interlocking results in not only a stronger bond, but also a more durable bond, because the interface does not rely solely on chemical bonds that may be broken with the infiltration of water.

Materials

The present durability study used 50-mil (1.27 mm) thick sheets of Ti-15Al-3Cr-3Sn-3Al (Ti-15-3 – a metastable β-alloy) in cracked-lap shear specimens. We examined three titanium surface treatments on the Ti-15-3 foils in this study: a) Sol-Gel, b) Turco 5578, and c) Pasa-Jell 107. Sol-Gel is a proprietary surface treatment developed by The Boeing Company for use in titanium bonding applications. It is a relatively new process, and it has shown good bonding strength on titanium. Turco 5578® (Elf Atochem North America, Philadelphia, PA) is a more mature surface treatment process that is used by the Lockheed-Martin Corporation. It has shown good resistance to moisture and high temperatures in several bonding applications. Pasa-Jell 107™ is a surface treatment that is used by NASA, and it also has shown good moisture resistance and good performance in high temperatures. We did not include more commonly used surface treatments such as Chromic Acid Anodizing (CAA), or Phosphoric Acid Anodizing (PAA), because of the environmental regulations that may restrict the future use of many of these processes.

After applying the various surface treatments, the titanium would be covered with the adhesive primer BR5® (Cytec Industries, Havre de Grace, MD). This primer was applied because of the limited lifetime of the surface treatments. Each surface treatment had a specified time on the order of 24 hours or less that it could be exposed to the environment before it would be rendered useless. Therefore, the standard practice of applying a primer to the treated titanium was used. The primer BR5 is a 20% solution of a polyimide in the solvent N-methyl-2-pyrrolidinone (NMP). The titanium plies, with the primer applied, would then be assembled at NASA-Langley into composite panels.

In addition to comparing the candidate surface treatments, this study also investigated the difference between two high-performance polyimides, FM5® and LaRC-IAX. FM5® (Cytec Industries, Havre de Grace, MD) and LaRC™-IAX (NASA-LaRC) have both shown very good results in earlier studies. Also, this is one of the first studies to give a direct comparison between these two adhesives.

Adhesives

Because of the high temperatures that the HTCL would experience during its service life, and also because of the desire to maximize adhesive toughness for a durable bond, polyimide-based adhesives were chosen for this application during the early stages of HTCL development. Researchers at NASA-Langley Research Center developed the first polyimide included in this project, designated LaRC™-IAX. More precisely designated as a copolyimide, LaRC™-IAX is formed from a reaction between 4,4′-oxydiphthalic anhydride (ODPA) with a diamine blend of 75 to 90 mole percent of 3,4′-oxydianiline (3,4′-ODA) and about 10 to 25 mole percent of para-phenylene diamine (p-PDA). The polymer backbones found in the copolyimide are given in Figure 2. Its glass transition temperature (Tg) varies with the cure temperature, ranging from a Tg of 236.8°C at a cure temperature of 300°C up to a Tg of 268.0°C at a cure temperature of 400°C [10]. This copolyimide has shown improved solvent resistance over other polyimides, while maintaining its adhesive properties in high-temperature lap shear tests.

The other polyimide included in this investigation is designated FM5®, which is produced by Cytec Industries, Incorporated. FM5® is

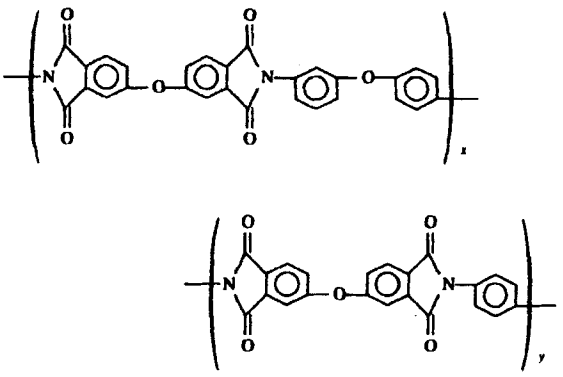

FIGURE 2 Repeat units of LaRC™-IAX where x ranges from 75 to 90 mole percent, and y ranges from 10 to 25 mole percent.

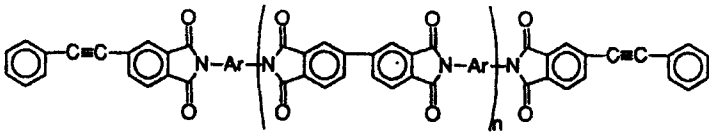

FIGURE 3 Repeat Unit of PETI-5 polyimide. FM5® is a blend of approximately 70% PETI®-5 and 30% LaRC™-IAX.

also a copolyimide, comprised of a blend of roughly 70% PETI-5 and 30% LaRC™-IAX; the structures of these polyimides are given in Figure 3. PETI-5 is another polyimide that was developed at NASA-Langley for high-temperature aerospace applications, such as the High Speed Civil Transport. PETI is an acronym that stands for PhenylEthynyl-Terminated Imide. PETI-5 results from the reaction of 3,3′,4,4′-biphenyltetracarboxylic dianhydride blended into an 85:15 ratio of 3,4′-oxydianiline and 1,3-bis(3-aminophenoxy) benzene with 4-phenylethynylphthalic anhydride as the terminating agent.

PETI-5 follows a pattern similar to LaRC™-IAX for its glass transition temperature. The Tg for PETI-5 ranged from 210°C, at an annealing temperature of 250°C, up to a Tg of 270°C for an annealing temperature of 350°C [11]. Certain processing steps can produce PETI-5 in an amorphous form in addition to its semi-crystalline form.

These two polyimide adhesives were supplied on a fiberglass carrier cloth, commonly referred to as a glass scrim cloth. This was per the

manufacturers' assertion that the scrim cloth was necessary to produce a consistent, high-quality adhesive. Prior attempts by the manufacturers to generate a neat resin adhesive film (*i.e.*, only the polymer) with either of these polyimides resulted in very poor quality films. This fiberglass carrier cloth complicated the bond strength analysis in that there was another interface for the crack growth to follow in addition to the polymer/metal oxide and metal oxide/base metal interfaces. This scrim cloth interface would be the limiting factor in the strength of the adhesive layer, but other studies using similar polyimide adhesives demonstrated very good fatigue resistance and fracture toughness values, lessening the concern that any significant strength could be generated. Butkus [12] showed fracture toughness values of $1100\,J/m^2$ for titanium-based CLS specimens. From this information, failure along the scrim cloth interface was taken as a cohesive failure of the adhesive.

Surface Treatments

The Turco 5578 process is based on an alkaline cleaning solution that can also be used as an etchant at higher concentrations. It is comprised of sodium hydroxide, a mixture of di- and triethanolamines, and sodium gluconate. Wegman [13] classified the surface morphology produced by Turco 5578 as Group II, with an oxide thickness of approximately 175 Å. Group II oxides all possess a high degree of macro-roughness (relative to the other oxides). Wegman further characterized the Turco 5578-treated surface as having protrusions that extend several microns above the titanium surface, with fine structures on the order of $0.1\,\mu m$ evident on the surface. Natan *et al.* [14] reported a similar fine structure on Turco 5578-treated titanium. Natan *et al.*, found that the structure was primarily amorphous TiO_2; however, they also referenced conflicting reports that found the rutile structure of TiO_2 after Turco 5578® treatment.

The second titanium surface treatment investigated was the Sol-Gel process developed by researchers at The Boeing Company. Blohowiak *et al.* [15] detail the process as producing a gradient coating from the substrate metal surface through a zirconium oxide interfacial layer to a mixed silicon-zirconium region. An organic coupling group, typically an organosilane, compatible with the adhesive system to be used, is oriented towards the interface with the adhesive. This organosilane is

accompanied by an organic acid catalyst and an alkoxyzirconium stabilizer to help produce covalent bonds from the metal substrate all the way to the adhesive, thereby increasing the durability of the system.

The surface morphology of titanium after Sol-Gel treatment is similar to that seen for the Turco 5578® process. This similarity could be expected, since a Turco 5578® bath is a preliminary step in the Sol-Gel surface preparation of titanium components. The surface exhibits micro-roughness that follows the grain boundaries very closely. Teeth-like projections on the order of 0.1 – 0.2 μm cover the entire surface, with a high degree of organization of these projections occurring near grain boundaries. However, a definitive measurement of the total oxide thickness was not made for this project.

The Pass-Jell 107™ surface treatment has been used for several years in the adhesive bonding of titanium structures. Pasa-Jell 107™ is comprised of approximately 40% nitric acid, 10% combined fluorides, 10% chromic acid, and 1% coupling agents, with the balance water [16]. Wegman [13], as noted previously, classified the surface morphology as Group II, though it has a dramatically different appearance from the other two surface treatments included in this study. Its micro-roughness is approximately an order of magnitude larger than the fine structure generated from Turco 5578® or Sol-Gel. Instead of having a tooth-like appearance, these projections are randomly oriented and are of various shapes, reminiscent of frozen waves.

Specimen Design and Construction

This study utilized a cracked-lap shear (CLS) bonded joint specimen to quantify the adhesive strength of the polyimide-titanium bond. To simplify the analysis of the bond strength and durability, NASA-Langley manufactured CLS specimens for this study that did not include reinforcing carbon fibers. The cracked-lap shear specimen configuration was chosen because of its close approximation to bonds that are commonly found in aerospace structures, and also because of numerous prior studies that demonstrated the viability of this configuration. Other studies on the cracked-lap shear specimen have found that its design directs the applied force to the metal-adhesive interface very well. This will allow a better discrimination between the various polymers and surface treatments used. Primary design of the CLS specimen utilized the closed-form solution for this geometry, to

expedite the design of the specimens. This allowed a quick calculation of failure strengths for CLS specimens with various lamina thickness and number of laminae.

An effort was made during the design of the CLS specimens to keep the titanium foils close to the same thickness as the foils used in an HTCL. This was to minimize any possible differences in the surface structure produced by the three surface treatments on the titanium foil. From past processing experience, certain surface treatments would follow the surface grain orientation and geometry of the base metal very closely. With the grain orientation and geometry a direct result of the amount of work done to the metal, the amount of work done was increased as much as possible, which would minimize the thickness of the titanium foil. Therefore, the thickness of the titanium foil was minimized to allow a better representation of the surface structure that would be produced in an HTCL.

With the criterion of minimum titanium ply thickness established, the design process then focused on increasing the strength of the continuous section (strap) of the CLS specimen. The maximum strength required for the strap was assumed to be the load necessary to exceed the cohesive failure limit of the adhesive in the CLS geometry. The loads required were so large that the minimum titanium ply thickness was significantly greater than the 10 mils (0.25 mm) thickness used in initial HTCL layups. With the additional desire to minimize the amount of titanium used to produce the specimens, the final design settled on a continuous section (strap) comprised of three titanium plies of 50 mils (1.27 mm) thickness and a discontinuous section (lap) of one titanium ply. The final specimen dimensions are given in Figure 4.

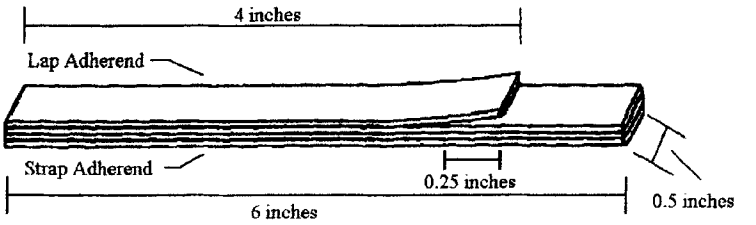

FIGURE 4 Cracked-lap shear specimen dimensions and geometry. Three titanium plies were used in the strap, with one titanium ply in the lap.

Once the general layup was determined from the closed-form solution, the specimen was modeled using the finite element code GAMNAS for a more precise analysis. GAMNAS was developed by researchers at NASA for modeling of test specimens such as the cracked-lap shear specimen used in this study. The geometry used for these cracked-lap shear specimens produced a G_I/G_{TOT} mode-mixity ratio of 0.20, and a G_{II}/G_{TOT} mode-mixity ratio of 0.80. GAMNAS also calculated the maximum stress generated in the CLS strap, so that the maximum testing load would not exceed the failure strength of a titanium ply. Also, GAMNAS was used to verify that the total strain energy release rate, G_{TOT}, remained constant for a given crack length. The finite element model revealed that G_{TOT} would remain within a band of ± 2 J/m^2 for the length of the specimen that would be used in the tests.

The fabrication of the CLS specimens presented a unique challenge because the three surface treatments were performed in three different locations. The Sol-Gel process was performed by The Boeing Company in Seattle, Washington; the Turco 5578 process was performed by Lockheed Corporation in their Charleston, South Carolina, facility; and NASA-Langley performed the Pasa-Jell 107™ surface treatment at their facility in Hampton, Virginia. The major difficulty arose because of the fact that the surface treatments had a certain time limit between treatment and bonding with the primer. Therefore, primer had to be shipped to each facility before the companies could perform their respective titanium surface treatment. After priming, the titanium sheets were wrapped, sealed, and shipped to NASA-Langley. The time frame between priming the sheets and final bonding in the CLS specimens was somewhat of an unknown variable. There were no available data on the maximum time between priming and final bonding with an adhesive, but a Boeing representative stated that a window of approximately two weeks would be safe for these adhesive primers [17].

The primer used on the titanium sheet was BR5®, manufactured by Cytec Industries, Inc. of Havre de Grace, Maryland. The BR5® primer, as mentioned previously, is a 20% solids solution of the PETI-5 adhesive in N-methyl-2-pyrollidone (NMP) solvent. This low viscosity solution is applied to freshly-treated titanium sheets, and then dried and cured following the procedure outlined by Cytec [18].

Once the primed and cured titanium sheets reached NASA-Langley, they were alternately layered with adhesive in the 3:1 ratio of

continuous (strap) plies to lap plies that was previously determined by closed-form solution and also by finite element modeling. The strap titanium sheets were 150 mm (6 inches) long by 200 mm (8 inches) wide, with the lap titanium sheet measuring 100 mm (4 inches) long by 200 mm (8 inches) wide. A piece of Kapton® film was placed approximately 6.5 mm (0.25 inches) from the ply edge between the lap ply and the first continuous (strap) ply to act as a starter crack. A schematic of the CLS panel dimensions, and the location of the Kapton film is given in Figure 5.

Once the titanium sheets and adhesive layers were arranged, the panels were sealed onto an autoclave tray, and a vacuum line attached to remove volatiles. The adhesive in each panel was then cured, following the prescribed cycles for FM5 and for LaRC™-IAX. After the autoclave curing cycle, the bonded titanium panels were then cut into specimens and shipped to Georgia Tech for testing and environmental exposure.

Long Term Exposure Environments

The present study examined the mechanical performance of these bonded systems in two aggressive environments that would be typical for high-speed aerospace applications. After consultation with NASA scientists, two environments were chosen that were projected to be the most damaging to the integrity of the adhesive bond. One environment

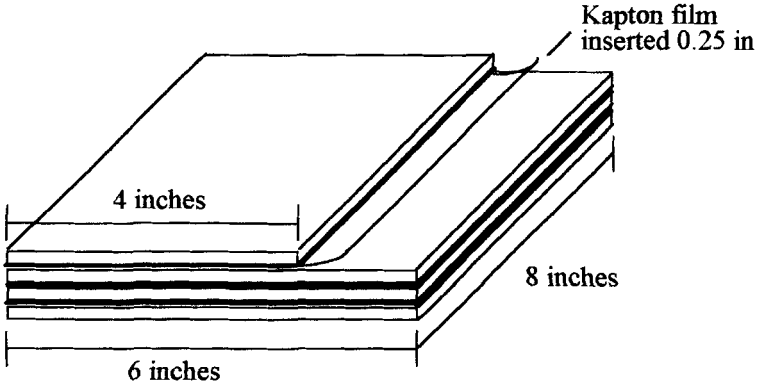

FIGURE 5 Dimensions of the Cracked-Lap Shear panels before cutting into specimens.

simulated the conditions found on sub-tropical airport runways, termed Hot/Wet, and the other environment simulated the temperatures found during prolonged supersonic flight, named Hot/Dry or simply Hot. The Hot/Wet environment subjected the titanium-polyimide bonded specimens to constant temperatures of 160°F (71°C) and greater than 95% relative humidity (RH), while the Hot/Dry environment exposed the specimens to constant temperatures of 350°F (177°C) and less than 10% RH.

The bonded specimens were subjected to these two environments for 5,000 hours and then tested under laboratory conditions of 70°F (21°C) and approximately 50% RH. The 5,000-hour time frame allowed a good comparison with previously-reported data on similar systems, but, most importantly, it gave an indication of the long-term performance of these adhesive systems under adverse conditions.

Mechanical Testing Prior to Exposure

Fatigue Crack Growth

With three titanium surface treatments and two polyimides, six specimen types were tested. First, the as received fatigue performance of each specimen type was evaluated at a variety of loadings to produce a (da/dN) *versus* ΔG graph. This graph gives an indication of the sensitivity of the bond to crack initiation and growth, and also of the minimum energy required to propagate a crack. The change in the total strain energy release rate was chosen for this comparison rather than the more traditional ΔK due to the heterogeneous nature of the bondline, following Ripling's leading role in analyzing bonded systems. Ripling *et al.*, recognized the need for a different variable other than K in bonded systems, and proposed the use of the more fundamental strain energy release rate, G, to describe fracture in adhesive joints [19].

The fatigue tests were conducted on two servo-hydraulic test frames that used the Testar family of operating programs. The initial tests were run on an MTS test frame with a load limit of 5 kips, but some of the adhesive systems required loads above 5 kips, so the remaining tests were run on an Instron test frame with a load limit of 20 kips. The cyclic load ratio was calculated to be at an R-ratio of 0.1 with respect to the total strain-energy release rate, G_{TOT}. In other words, the cyclic

loads would be calculated to give a 10-to-1 ratio of maximum-to-minimum total strain energy release rate. From earlier studies on a similar geometry, rough estimates of maximum stresses were determined for initiation crack growth up to Stage III crack growth rates. The crack growth rate (da/dN) used in this study as initiation was approximately 1×10^{-6} mm/cycle, and a da/dN of 1×10^{-3} mm/cycle was used as a rate approaching Stage III crack growth.

The results from these fatigue tests are shown in Figures 6 and 7. From these graphs, the FM5®/Sol-Gel system has the greatest resistance to crack growth, with the FM5®/Pasa-Jell 107™ also system performing well. The worst performer is clearly the LaRC™-IAX/Sol-Gel system. From analysis of the fracture surface of this system, the locus of failure was the primer-adhesive interface.

Fracture Toughness

After the fatigue data were collected, the fracture toughness was measured on each specimen by loading each of them in a quasi-static fashion. The fracture toughness data were collected after the fatigue data for two reasons: (1) there would be a sharp crack for the fracture

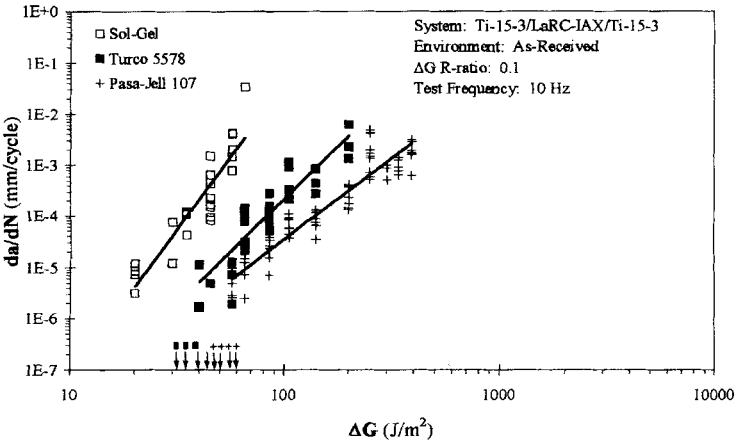

FIGURE 6 Comparison of fatigue crack growth response of CLS specimens with LaRC™-IAX polyimide adhesive and three titanium surface treatments that were exposed only to laboratory conditions, and tested under typical laboratory conditions of 70°F and 50% RH.

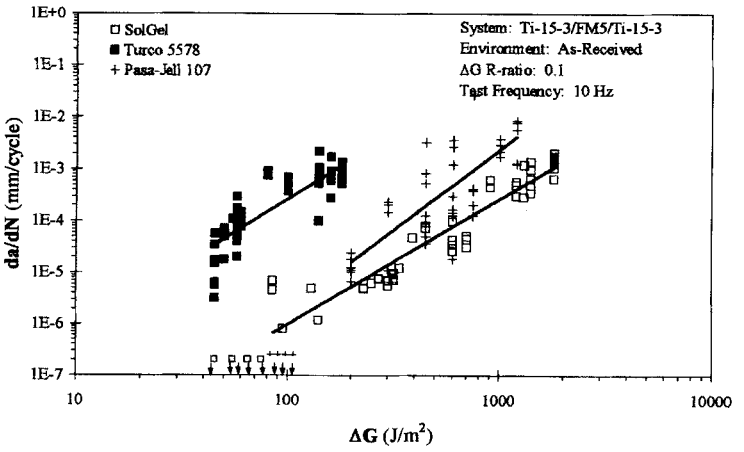

FIGURE 7 Comparison of fatigue crack growth response of CLS specimens with FM5® adhesive and three titanium surface treatments, tested under typical laboratory conditions of 70°F and 50% RH. Note higher required energy for crack growth, as compared with Figure 6.

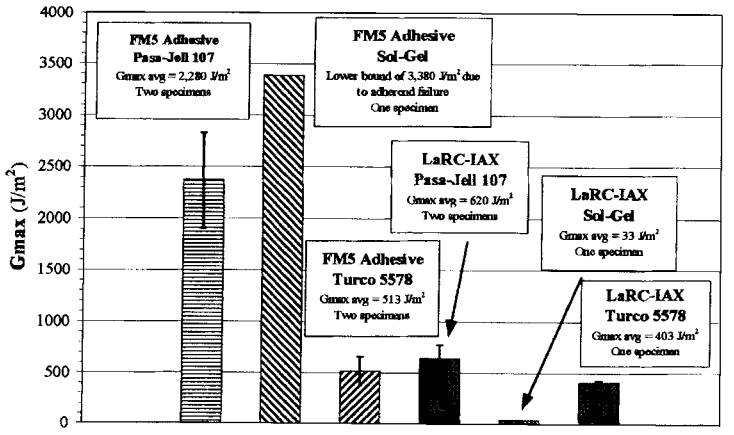

FIGURE 8 Fracture toughness of the six specimen types in the as-received condition (no exposure), tested under typical laboratory conditions of 70°F and 50% RH. Note that FM5®/Sol-Gel had the specimen fail prior to maximum load measurement and also that LaRC™-IAX/Sol-Gel specimen data are suspect.

toughness data, and (2) if the specimen catastrophically failed during fracture toughness testing, we would still have the fatigue data for that specimen. The results for each specimen type are given in Figure 8. The

loading rate was 100 (lbs/sec) (220 kg/sec), with the maximum load measured several times on the same specimen to ensure that the correct value was measured.

The FM5®/Sol-Gel specimen fracture toughness shown in Figure 8 is a lower bound for the toughness because the specimen failed prior to crack growth. Also, the LaRC™-IAX/Sol-Gel fracture toughness data are suspect due to almost instantaneous failure when a load was applied to the specimen. This occurred in both LaRC™-IAX/Sol-Gel specimens, so there appears either to be a problem in the processing or there is poor compatibility between the adhesive and the primer.

Mechanical Testing After Exposure

Fatigue Crack Growth

Using the same methodology utilized for the non-exposed specimens, after 5,000 hours of exposure specimens from both environments were tested at laboratory conditions of 70°F (21°C) and approximately 50% RH. This allowed a good comparison between the non-exposed specimens and the ones that had been exposed, without having to compensate for changes in performance if the fatigue and/or fracture toughness tests were performed at elevated temperature.

Because of the large volume of data generated in this study, only the best and worst systems will be detailed here. The results from these fatigue tests are given in Figures 9 and 10. From these graphs of the best- and worst-performing bonded systems, a large breadth in performance was found for these six systems. The FM5®/Sol-Gel system has the greatest resistance to crack growth, both before and after exposure to aggressive environments. The worst performer in the As-Received condition, the LaRC™-IAX/Sol-Gel system, performed poorly again after exposure, though it is important to note here that the three LaRC-IAX-based systems performed so poorly that it was difficult to differentiate among their performances. The other four systems fell within these two extremes, roughly in the same order as for the As-Received data given in a previous section.

Fracture Toughness

Again, the fracture toughness data were collected in a similar fashion as for the As-Received, or non-exposed, specimens. The data for both

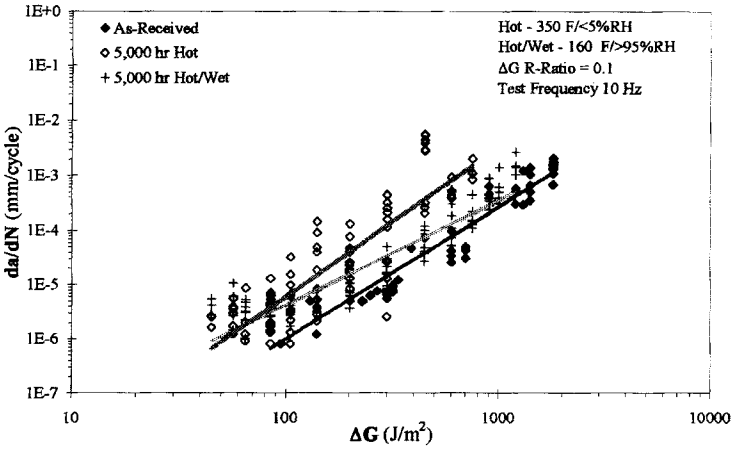

FIGURE 9 Fatigue data of the best-performing bonded system in the study. Mixed-mode behavior of CLS specimens made with FM5® adhesive and Sol-Gel surface treatment tested as-received, subjected to Hot/Wet (160°F/ > 95% RH), and Hot (350°F/ < 5% RH) exposures.

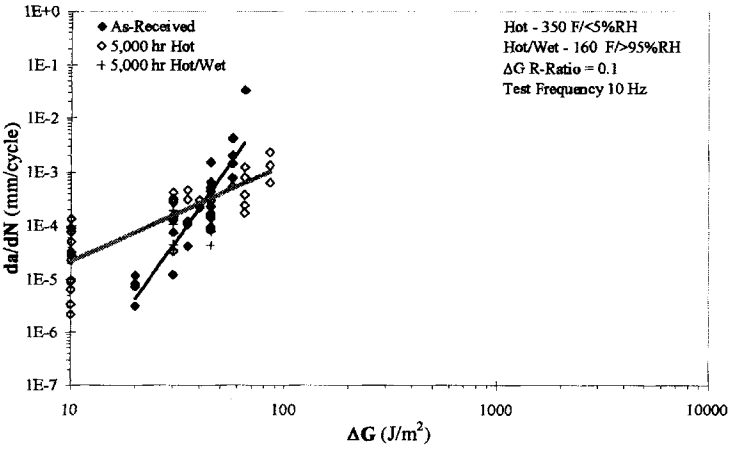

FIGURE 10 Fatigue data of the worst performing bonded system in the study. Mixed-mode behavior of CLS specimens made with LaRC™-IAX adhesive and Sol-Gel surface treatment tested as-received, subjected to Hot/Wet (160°F/ > 95% RH), and Hot (350°F/ < 5% RH) exposures.

types of exposed specimens, along with the data for the As-Received specimens, are given in Figure 11. Unlike the fatigue data, the fracture toughness of these systems could be condensed into one clear graph,

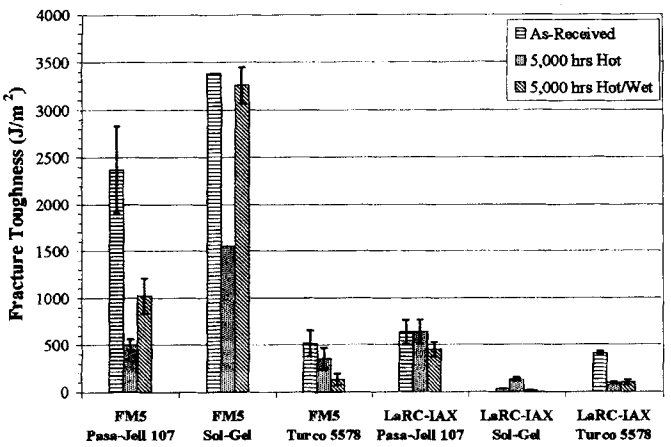

FIGURE 11 Fracture toughness of cracked-lap shear specimens made with two polyimide adhesives and three surface treatments, tested as-received and tested after exposure to Hot/Wet or Hot/Dry environments. Error bars represent the 95% confidence interval for the tests that had a sufficient number of data points for the calculation.

giving a clear order to their overall performance. As can be seen in Figure 11, there is a significant distinction between the LaRC™-IAX systems and the FM5® systems. Within the three FM5® systems, the Sol-Gel specimens performed significantly better than any other specimen type, demonstrating a fracture toughness two to three times greater than that of the next-best bonded system after 5,000 hours in either exposure environment. The LaRC™-IAX systems did not perform well at all after exposure, which was not surprising considering their poor As-Received performance.

FRACTURE ANALYSIS

After the fracture toughness data were collected for each specimen, the specimens were frozen (< 30°F) (−1°C) and then the lap was completely separated from the strap to allow an investigation into the locus of failure for each specimen. This was carried out in the hopes of correlating the fatigue and fracture toughness data to the failure mode of each specimen. There were three failure modes found in these CLS specimens: (1) metal oxide/adhesive interfacial failure,

(2) cohesive failure of the adhesive, including failure at the scrim cloth, and (3) primer/adhesive interfacial failure.

The first two are widely accepted as valid failure modes. The third failure mode, failure along the primer/adhesive interface, came after analyzing several fracture surfaces visually and with the aid of an optical microscope. Fracture surfaces such as that given in Figure 14 illustrate the need for a third failure mechanism, other than the standard metal oxide/primer interfacial failure plane and the cohesive failure of the adhesive. The smooth appearance of the adhesive layer, with adhesive appearing on both fracture surfaces, indicates that an interfacial type of failure occurred within the adhesive layer, which can be best explained by some type of poor interaction between the primer and the adhesive. This explanation is not given to be the definitive answer for this type of failure-much more work would have to be performed before any solid conclusion could be drawn. This third mechanism of primer/adhesive interfacial failure is used to give a working model to fit the fatigue and fracture toughness data to the fracture surfaces.

The lowest strength specimens, which were the Sol-Gel/LaRC™-IAX specimens, displayed a failure at the primer/adhesive interface during high cycle fatigue, which indicates a poor interaction between the primer and the adhesive at the interface. This is most likely a processing (or blending) problem for those two polyimides, which can be due to a large surface energy barrier or an incompatibility between the molecular species responsible for bonding. During low-cycle fatigue and fracture toughness testing, the crack tip moved away from the lap primer/adhesive interface towards the adhesive/scrim cloth interface, which is more in the center of the bondline. The specimen tested in the As-Received condition (*i.e.*, no exposure) is shown in Figure 12.

The specimens exposed to the Hot environment displayed a similar fracture path to the As-Received specimens. These specimens failed almost exclusively along the primer/adhesive interface, though the failure plane changed somewhat to the scrim cloth/adhesive interface during fast fatigue crack growth and also during fracture toughness tests. A representative fracture surface is shown in Figure 13.

The Hot/Wet exposed specimens performed so poorly in the mechanical analysis portion of this project that it was virtually

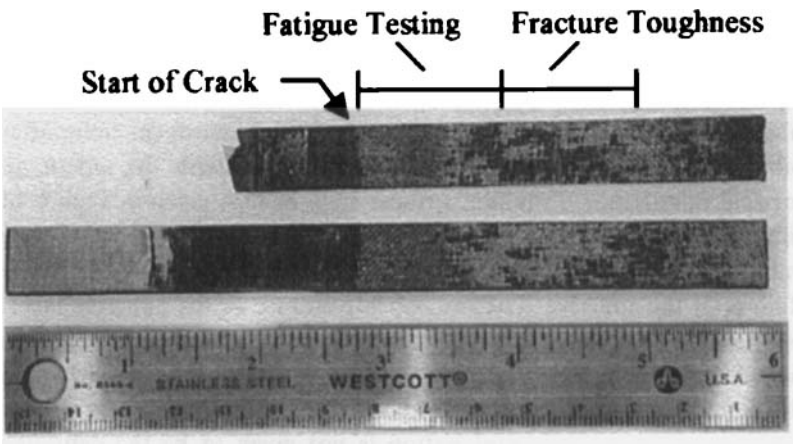

FIGURE 12 Failure of the lowest fracture toughness and least fatigue-resistant system (Sol-Gel and LaRC™-IAX) occurred along the primer and adhesive interface. This specimen was in the as-received condition, with no environmental exposure. The regions tested during each type of measurement are shown, with the crack progressing from left to right.

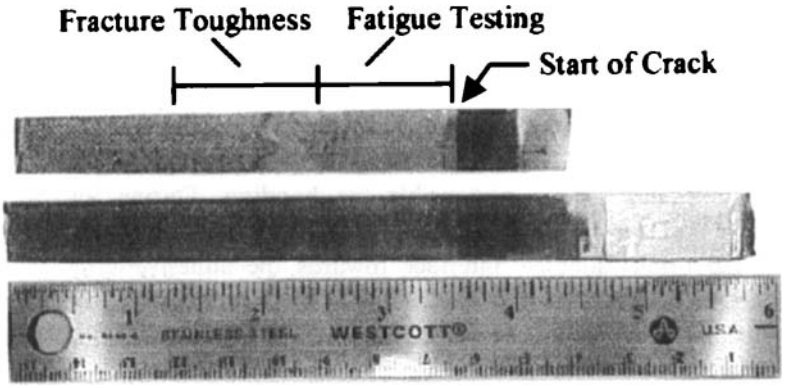

FIGURE 13 Failure for the LaRC™-IAX/Sol-Gel after 5,000 hours of exposure in the Hot environment occurred primarily at the primer/adhesive interface. Note that the locus of failure changed to the adhesive/scrim cloth interface during fracture toughness testing.

impossible to collect fatigue data or fracture toughness data on the specimens. These specimens would completely debond with only a small amount of applied load. Due to the fact that no specimen of this

bonded system displayed any substantial strength or fatigue resistance, it is difficult to distinguish physically any differences in the failure modes for the three exposed sets. Therefore, the failure mode appears to be very similar to the other environments, as seen in Figure 14. However, one slight difference between the three types of fracture surfaces is that the Hot/Wet fracture surface was smooth, indicating a poor bonding action between the primer and the adhesive.

The highest fracture toughness specimens, which also displayed the best fatigue resistance, were the FM5®/Sol-Gel specimens. These specimens failed along the plane of the scrim (carrier) cloth that was used in the adhesive layer. This indicates that the titanium/primer/adhesive interfacial bonds were stronger than the bonding between the adhesive and the glass-fiber scrim cloth. A sample failure surface is given in Figure 15.

After 5,000 hours of exposure in the Hot (350°F/< 5% RH) environment, the fracture surface still exhibited failure at the scrim cloth/adhesive interface. However, there was a substantial amount of failure that occurred at the adhesive/primer interface. Optical microscope observations also indicate some debonding occurring at the surface treatment/primer interface in these regions. The adhesive/primer and primer/surface treatment debonded areas can be seen as dark areas from the area around 1 inch and also the region around 3.5 inches on the scale in Figure 16.

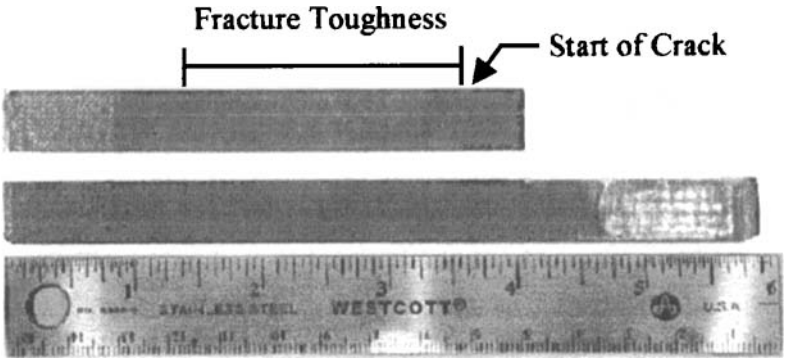

FIGURE 14 Failure for LaRC™-IAX/Sol-Gel after 5,000 hours of exposure in the Hot/Wet environment occurred exclusively at the primer/adhesive interface. No conclusive fatigue data could be collected on these specimens.

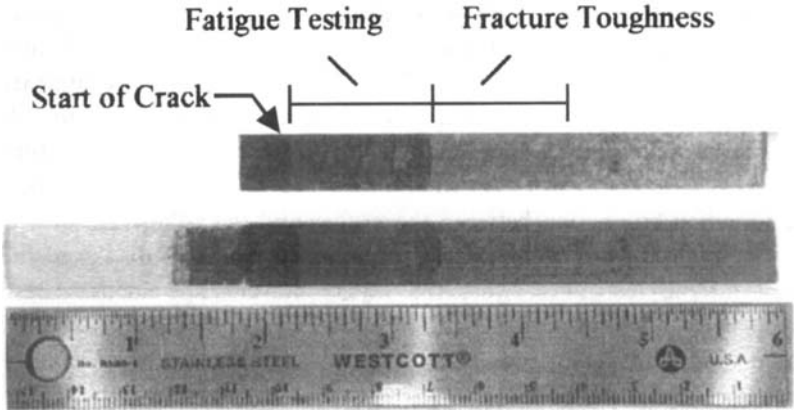

FIGURE 15 Failure of the highest fracture toughness and best fatigue resistant specimen (Sol-Gel and FM5®) occurred between the adhesive and the scrim (carrier) cloth in the adhesive layer, regardless of the type of test performed. This specimen was in the as-received condition, with no environmental exposure.

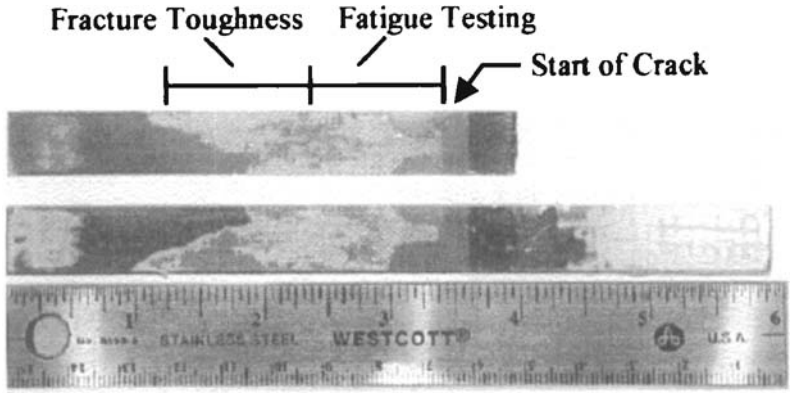

FIGURE 16 Failure of the FM5®/Sol-Gel bonded system after 5,000 hours exposure in the Hot environment occurred predominantly at the scrim cloth-adhesive interface. Substantial debonding also occurred at the primer/adhesive and the primer/surface treatment interfaces.

The specimens exposed to the Hot/Wet environment for 5,000 hours displayed the same failure mode as the As-Received specimens. Figure 17 shows that the entire failure surface was at the scrim cloth/adhesive interface, which correlates well with the fatigue data and the fracture toughness data.

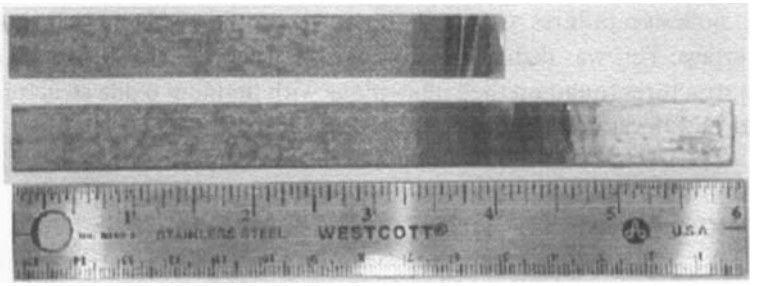

FIGURE 17 Failure of the FM5®/Sol-Gel bonded system after 5,000 hours exposure in the Hot/Wet environment occurred exclusively at the scrim cloth/adhesive interface.

The figures in this section illustrate the overall pattern found in the fracture surfaces of the specimens; namely, that specimens exposed to the Hot/Dry environment showed increased amounts of interfacial failure over the As-Received or Hot/Wet exposed specimens. This indicates that the bonds originally present in these systems are being weakened or broken due to the increased energy available from the elevated temperature environment. According to St. Clair [20], the bonds most likely being broken are the ones between the bonding agents used in the Sol-Gel surface treatment and the polyimide adhesive. Work performed by Butkus [12] indicates that the polyimide adhesive itself is not degrading in bulk, so the degradation must be occurring at an interface.

Determining the plane of adhesive failure for the other material systems is complicated because of the presence of the titanium oxide layer which was generated by the titanium surface treatment. Adhesive failure can occur between the titanium substrate and the titanium oxide layer, or it could occur between the titanium oxide layer and the adhesive primer, or it could occur between the adhesive primer layer and the bulk adhesive. Precise determinations of the adhesive failures need other analysis techniques than just the optical techniques used in this study. However, observations give strong indications as to the plane of failure, along with a careful analysis of the mechanical performance of the systems.

All four remaining systems had observable adhesive failure for all exposure environments, though not to the degree seen for the FM5®/ Sol-Gel system. Optical microscope observations indicate that most of

the adhesive failures occurred at, or near, the oxide layer/primer interface. This was deduced by comparing the color and the texture of the structures found on the failure plane with titanium oxide structures that had never been bonded.

CONCLUSIONS

This research determined the best combination of commercial surface treatment and polyimide adhesive from the six bonded systems analyzed. These six systems compared three surface treatments that are considered to be more environmentally-friendly than chromic acid anodizing (CAA), and two polyimide adhesives that are formulated to contain fewer carcinogenic species. For the as-received specimens analyzed, this study found that the Sol-Gel surface treatment used in conjunction with the FM5® adhesive produced the greatest fracture toughness (greater than 3400 J/m^2), along with the best fatigue crack growth resistance of any of the six systems analyzed. The FM5®/Sol-Gel system also retained the most strength after exposure to the two long-term exposure environments (1500 J/m^2 and 3200 J/m^2 for the Hot/Wet and the Hot/Dry, respectively). The Pasa-Jell 107™ FM5® system also performed well in fracture toughness and fatigue testing, though not as well as the Sol-Gel/FM5® system.

The cracked-lap shear specimen was a good specimen choice for this study, due to the tendency of the crack tip to concentrate the applied stress at the interface between the plies. The design of the CLS specimens worked well, except for the highest strength specimens (Sol-Gel/FM5® system), which cracked the titanium plies at the maximum reported loading.

The Sol-Gel/LaRC™-IAX adhesive system performed surprisingly poorly during testing. This poor performance is most likely due to some type of unexpected interaction between the BR5 primer and the LaRC™-IAX adhesive. This occurred in both specimens, so there appears to be a problem in the processing, poor compatibility between the adhesive and the primer or the creation of a weak boundary layer between the two materials. The mechanical tests supported this speculation with the failure plane occurring at the interface between the adhesive and the primer.

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